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<b>(21) International Application Number:</b> PCT/US00/10824 <b>(22) International Filing Date:</b> 24 April 2000 (24.04.00)  <b>(30) Priority Data:</b> 60/131,560                      29 April 1999 (29.04.99)                      US 09/468,958                      22 December 1999 (22.12.99)                      US  <b>(71) Applicant (for all designated States except US):</b> IMERYS PIGMENTS, INC. [US/US]; 100 Mansell Court East, Suite 300, Roswell, GA 30076 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> LYONS, Anthony, V. [US/US]; 140 Saddle Run Ct., Macon, GA 31210 (US). ZHANG, Zhichao, R. [-/US]; 342 Log Cabin Road, Apt. 10G, Milledgeville, GA 31061 (US).  <b>(74) Agents:</b> GARRETT, Arthur, S. et al.; Finnegan, Henderson, Farabow, Garrett & Dunner, L.L.P., 1300 I Street, N.W., Washington, DC 20005-3315 (US).		<b>(81) Designated States:</b> AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PIGMENT COMPOSITION FOR PAPER COATING, PAPER COATING USING THE SAME AND METHOD OF COATING PAPER		
<b>(57) Abstract</b> <p>A pigment composition for use in coating a paper product such as a solid bleached sulfite product to give a combination of improved sheet brightness and gloss, comprises a blend of at least two particulate inorganic materials namely (a) a high brightness ultrafine kaolin produced from a blocky kaolin clay, the kaolin having a median particle size less than about 0.5 microns (<math>\mu\text{m}</math>); and (b) a fine coating precipitated calcium carbonate (PCC), which may be of predominantly aragonite or rhombohedral crystal form, having a median particle size less than about 0.8 microns; the ratio by weight of the PCC to the kaolin being greater than 1.0.</p>		

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-1-

## TITLE OF THE INVENTION

PIGMENT COMPOSITION FOR PAPER COATING, PAPER COATING USING  
THE SAME AND METHOD OF COATING PAPER

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This application claims the benefit of U.S. Patent Application No. 09/468,958, filed December 22, 1999, and U.S. Provisional Application No. 60/131,560, filed April 29, 1999.

## 10 BACKGROUND TO INVENTION

## 1. Field of the Invention

The present invention relates to a pigment composition for use in paper coating, a paper coating composition containing the same and a method of coating  
15 paper using the same.

The properties of coated paper products, including paper sheet, packaging and board products, depend heavily on the formulation of the coating applied to the paper, especially the pigments employed in the coating  
20 formulation. For some products, eg coated freesheet paper and coated solid bleached sulfite (SBS) board, sheet brightness is the most significant optical property required by manufacturers and users although other optical properties such as sheet gloss may also be  
25 important to a lesser extent. In order to produce high sheet brightness in such products manufacturers, especially in North America, have previously used blends of fine kaolin with fine calcium carbonate in compositions for use in coating such paper products. The  
30 main purpose of the present invention is to provide a

-2-

novel pigment composition of this kind giving an improved combination of coating properties.

## 2. Summary of the prior art

In the prior art, pigment blends of kaolin and calcium carbonate for use in coating compositions have conventionally been prepared from ground calcium carbonate and kaolin typically with a high kaolin content in the blend. The level of calcium carbonate employed in such blends has in many cases been less than 50% of the pigment weight. However methods have been sought to improve the coated sheet brightness of paper product sheets coated with compositions containing such pigment blends.

Although optical brightening agents (OBA's) may be used to give an increase in observed sheet brightness from kaolin-containing coatings use of such agents is desirably avoided in many materials, especially those designed for packaging applications, since such agents generally are not approved by regulatory authorities such as the US Food and Drugs Administration (FDA).

It has been found in a number of instances to be desirable to use a higher calcium carbonate content in kaolin/carbonate blends since calcium carbonate can be produced more cheaply than kaolin and has a greater powder brightness than kaolin and this can provide a greater contribution to sheet brightness. In some previously used formulations attempts have therefore been made to employ higher carbonate contents in kaolin/calcium carbonate blends. However it has been

found that these previously used formulations are unsatisfactory as the resulting sheet gloss is lower than is desirable. In order to improve the sheet gloss for a given kaolin/carbonate blend, conventionally the level of 5 carbonate in the blend has to be reduced, which accordingly reduces the brightness of the coated paper or else high calendering pressure is required during the finishing stage which brings with it a cost penalty.

Plastic pigments may be used to avoid reducing the 10 gloss without a reduction in the calcium carbonate level or an increase in the calendering pressure. However, these pigments are costly and their use also causes an increase in the cost of the coating formulation.

The present invention aims to produce a novel 15 carbonate-rich pigment composition of calcium carbonate and kaolin which does not cause a significantly reduced gloss when used in a coating formulation to provide a coating on a paper product, thereby advantageously reducing the need to employ plastic pigments or high 20 calendering pressures and therefore bringing with it significant economic benefits.

Another important property of the coating formulation is binder demand. Packaging products in particular have a high binder demand and it is desirable 25 to take steps to reduce this wherever possible in order to reduce the cost of the coated product. The binder demand is determined by the pigment specific surface area. The binder demand is lower for pigments of lower specific surface area.

-4-

Thus, the objects of the invention are to produce a pigment composition useful for coating paper and board products, especially packaging products, giving an improved combination of sheet brightness and sheet gloss and which may also have reduced coating binder demand. These and other objects which will become apparent hereinafter are fulfilled by the present invention.

US Patent No. 5833747 describes blends of aragonite PCC and platey kaolin. The present invention employs a composition comprising a blocky rather than a platey kaolin which together with a PCC, both of selected median particle size in a selected carbonate-rich formulation, produces a sheet brightness and gloss which are both considerably higher than those reported in this prior art patent.

#### SUMMARY OF THE PRESENT INVENTION

The present invention aims to produce a pigment composition for use in a coating composition for coating paper products which produces a coating structure on the paper product that yields an improved combination of brightness and gloss and in some cases printability.

According to the present invention in a first aspect there is provided a pigment composition for use in coating a paper product, comprising a blend of at least two particulate inorganic materials comprising (a) a high brightness ultrafine kaolin produced from a blocky kaolin clay the kaolin having a median particle size less than about 0.5 microns ( $\mu\text{m}$ ) and (b) a fine coating precipitated calcium carbonate (PCC) having a median particle size less than about 0.8 microns, the ratio by

-5-

weight of the PCC to the kaolin being greater than 1.0. The PCC may have a selected crystal morphology, for example a predominantly aragonite or rhombohedral morphology.

5       According to the present invention in a second aspect there is provided a coating composition comprising an aqueous suspension comprising the pigment composition of the first aspect and a water borne binder.

          According to the present invention in a third aspect  
10 there is provided a method for coating a paper product by applying the coating composition of the second aspect to coat a surface of the paper product.

          According to the present invention in a fourth aspect there is provided a method of improving the  
15 optical and printing properties of a paper product, comprising applying the coating composition of the second aspect to at least one surface of said paper product.

          For the purposes of the present invention the term 'paper product' includes paper sheets, paper packaging  
20 and board products and the like. The paper product to be coated according to the present invention may be uncoated or it may carry one or more previously applied coating layers.

#### DESCRIPTION OF THE PRESENT INVENTION

25       Surprisingly, it has been found that by combining the high brightness ultrafine kaolin (a) with the PCC (b) which may be predominantly of a selected morphology, in the compositions of the invention both the sheet brightness and sheet gloss of resulting coated paper  
30 products may be surprisingly and beneficially boosted to

-6-

a combined extent not obtained in the prior art for carbonate-rich calcium carbonate/kaolin blends

The composition according to the first aspect has a weight ratio of PCC to kaolin of greater than 1:1, preferably from 5:4 to 10:1, especially 3:2 to 4:1.

The kaolin and the PCC in the composition of the invention both have a small specified median particle size. The median particle size of an inorganic pariculate material is the particle equivalent spherical diameter ("esd") value less than which 50% of the particles have an esd. This is also referred to as the  $d_{50}$  value and may be measured in the manner described later.

The kaolin may beneficially have a median particle size of less than about 0.3 microns, especially between about 0.10 microns and about 0.25 microns, eg between 0.15 microns and 0.25 microns, eg about 0.2 microns.

The PCC has a median particle size of less than about 0.8 microns, and this may be between about 0.2 and about 0.7 microns, eg between about 0.25 microns and about 0.45 microns.

We have found, for example, that carbonate-rich blends of fine kaolin and fine aragonite or rhombohedral PCC unexpectedly produce favorable combinations of coated sheet brightness and gloss.

The kaolin employed in the present invention may comprise in addition to kaolinite as a major component one or more minor impurity minerals, eg clay minerals of the smectite group which comprises bentonite, montmorillonite, hectorite, beidellite and saponite or of



-7-

the kandite group, which comprises dicktite, nacrite and halloysite as well as kaolinite. Kaolinite containing minerals include china clays, kaolin type clays, ball clays and fire clays. For the purposes of the present invention, a kaolin clay is defined as a clay containing at least 90% by weight, preferably at least 95% by weight kaolinite.

The kaolin employed in the present invention may have been treated by one or more processes which are well known to those skilled in the art, for example by known refining or beneficiation steps. For example the kaolin clay may be bleached with a reductive bleaching agent, such as sodium hydrosulfite.

Without wishing to be bound by any particular theory we believe that the high performance characteristics of the pigment composition according to the first aspect of the invention are a result of the high pore volume that may be generated in the coating because of the unique particle size and shape of the pigments associated with both the kaolin (a) and the PCC (b). The large pore volume and radius are responsible for efficient light scattering which in turn provides high coating sheet brightness. The blend of fine pigments beneficially creates a microscopically smooth surface which significantly improves the sheet gloss.

The kaolin in the compositions of the present invention may be a fine glossing kaolin, e.g. it may be a kaolin which when used as a coating pigment may produce a smooth surface on a coated paper product, eg it may have a high proportion of fine particles, eg it may have

-8-

greater than 50%, e.g. greater than 60%, by weight of its particles having an esd less than 0.25 microns.

The unusual particle size properties of the kaolin and PCC as employed in the composition according to the first aspect may be illustrated by the particle size distribution ("psd") of these pigments. In this specification all pigment psd and median particle size measurements are as measured in a well known manner by sedimentation of the pigment in a fully dispersed condition in an aqueous medium using a SEDIGRAPH 5100 machine as supplied by Micromeritics Corporation. Such a machine provides measurements and a plot of the cumulative percentage by weight of particles having an esd less than given esd values.

15 The kaolin employed in the pigment composition of the present invention may have in the fully dispersed state a particle size distribution such that the percentage P by weight of particles having a size less than  $x\mu\text{m}$ , where x is respectively  $2\mu\text{m}$ ,  $1\mu\text{m}$ ,  $0.5\mu\text{m}$  and  $0.25\mu\text{m}$  is as follows:

25	<hr/>	
	x ( $\mu\text{m}$ )	P (%)
	2	at least 95
	1	at least 93
	0.5	at least 85
	0.25	at least 50
<hr/>		

In particular, the kaolin employed in the composition of the present invention may have the particle size distribution as follows:

-9-

	X (um)	P (%)
	2	at least 99
	1	at least 98
	0.5	at least 93
5	0.25	at least 68

The median particle size may be measured by such an analysis and for the fine kaolin employed in the composition of the invention may be less than 0.2 10 microns, e.g. between 0.10 and 0.19 microns.

The PCC employed in the present invention may, if predominantly aragonite, have in the fully dispersed state a particle size distribution such that the percentage P by weight of particles having a size less 15 than  $x\mu\text{m}$ , where x is respectively  $2\mu\text{m}$ ,  $1\mu\text{m}$ ,  $0.5\mu\text{m}$  and  $0.25\mu\text{m}$  is as follows:

	x ( $\mu\text{m}$ )	P (%)
20	2	At least 92
	1	At least 75
	0.5	At least 60
	0.25	Between 15 and 40

25 e.g. the PCC employed in the present invention may have the particle size distribution as follows:

	x ( $\mu\text{m}$ )	P (%)
	2	at least 95
30	1	at least 82
	0.5	at least 66
	0.25	between 23 and 33

-10-

Alternatively, the PCC employed in the compositions of the present invention may, if predominantly rhombohedral, have in the fully dispersed state a particle size distribution such that the percentage P by weight of particles having a size less than  $x\mu\text{m}$ , where  $x$  is respectively  $2\mu\text{m}$ ,  $1\mu\text{m}$ ,  $0.5\mu\text{m}$  and  $0.25\mu\text{m}$ , is as follows:

10

X ( $\mu\text{m}$ )	P (%)
2	at least 93
1	at least 86
0.5	at least 22
0.25	Between 5 and 25

15

e.g. the PCC employed in the compositions of the present invention may have the particle size distribution as follows ( $x$  and  $P$  as defined above):

20

x ( $\mu\text{m}$ )	P (%)
2	at least 97
1	at least 90
0.5	at least 25
0.25	between 7 and 17

25

The median particle size of such a rhombohedral PCC may be from about 0.4 to about 0.6 microns.

The kaolin employed in the compositions of the present invention may be a kaolin having a high brightness, eg a GE powder brightness of at least 85, e.g. at least 90.

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-11-

The PCC employed in the compositions of the invention may have a GE powder brightness of at least 90, e.g. at least 92.

The kaolin employed in the compositions of the present invention may be obtained from a relatively blocky kaolin clay, eg obtained from a secondary kaolin deposit such as from South East USA, e.g. from Georgia. Such kaolin clays usually have a relatively low shape factor. "Shape factor" as used herein is a measure of an average value (on a weight basis) of the ratio of mean particle diameter to mean particle thickness for a population of particles of varying size and shape as measured using the electrical conductivity method and apparatus described in GB-A-2240398/US-A-5128606/EP-A-0528078 and using the equations derived in these patent specifications. "Mean particle diameter" is defined as the diameter of a circle which has the same area as the largest face of the particle and is substantially the same as the median particle as defined earlier. The shape factor of the kaolin employed in the composition of the invention may for example be less than 20, e.g. less than 15, eg less than 12, especially less than 10, eg less than 9, eg 8 or less. By employing a relatively blocky kaolin rather than a platey kaolin in the present invention it is possible to produce runnable coating formulations or compositions having a higher solids concentration.

Calcium carbonates are known to precipitate in different crystal morphologies and the PCC used in the compositions and method of the present invention may

-12-

comprise any one or more of these morphologies. PCC is known to exist in the aragonite (aragonitic) form in which the crystals are needle shaped or in the calcite (calcitic) form. Various sub-classes of these two forms are referred to in the art. For example reference is often made to two main versions of the calcite form, namely rhombohedral in which the crystals have a rhomboid shape and scalenohedral in which the crystals have a kite shaped or double pyramid structure which favours twinning and growth of clusters. X-ray diffraction allows the aragonite and calcite forms to be distinguished and electron microscopy allows the rhombohedral and scalenohedral forms of the calcite form to be distinguished.

15 The aragonite form crystallises as long, thin needles generally having a length:diameter ratio of about 10:1. The length to diameter ratio of the crystals of the selected form, if predominantly aragonite, may for example average at least 5:1.

20 As is known to those familiar with the PCC art, the crystal form(s) obtained in the production of PCC depends upon a number of factors which have a complex relationship, such as the quantities and types of liquid, gaseous and solid species present, the temperature and, where the source of carbonate ions comprises CO<sub>2</sub> gas, the gas application rate. The result is that it is common to produce together a mixture of different crystal forms. The PCC form achieved in practice is unlikely to be 100% of the selected form. It is quite usual for one PCC crystal form even when predominant to be mixed with other

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-13-

forms. Such mixed forms can give suitably improved product properties. We prefer that the PCC is produced by a controlled process providing that at least 50% by weight, desirably at least 75% by weight of the crystals in the PCC to be employed in the pigment composition of the present invention are of a selected crystal morphology.

The PCC employed by the present invention may therefore be predominantly of an aragonite morphology. 10 For example, at least 50%, e.g. at least 75%, of the PCC may be of the aragonite crystal form.

The PCC employed by the present invention may alternatively be predominantly of a rhombohedral morphology, For example, at least 50%, e.g. at least 75%, 15 may be of the rhombohedral crystal form.

The process conditions during the precipitation process required generally to achieve principally a selected PCC crystal morphology, eg an aragonitic or rhombohedral morphology, and a selected median particle 20 size, are known to those skilled in the art and are described for example in the literature, e.g. in ----.

The pigment composition according to the first aspect of the present invention may be added to additional pigments, e.g. any of those known in the art 25 for use in coating applications. The blend of kaolin (a) and PCC (b) defined earlier may constitute 90% or more, in some cases 100% of the pigments present in the composition.

The pigment composition of the invention may be 30 formed by blending dry kaolin and dry PCC or it may be

formed using an aqueous suspension of one or both of the kaolin and the PCC.

The binder employed in the coating composition according to the second aspect of the present invention, defined earlier, may comprise one or more binders or adhesives known and/or used in the paper product coating art, for example it may comprise a waterborne binder such as selected from (i) waterborne natural and synthetic polymeric latices; (ii) polysaccharides such as starch and starch derivatives, and (iii) proteinaceous materials.

Where a latex is employed, the latex may comprise for example a styrene butadiene, acrylic latex, vinyl acetate latex, or a styrene acrylic copolymers. Where a starch is employed, the starch may comprise material derived from maize, corn or potato.

Examples of other suitable binders or binder components include casein and polyvinyl alcohol.

The binder may be used, on an active basis, in an amount of from 0.1% to 30% by weight, eg from 1% to 25%, especially from 4% to 20%, e.g. from 10% to 18%, based on the dry weight of the inorganic material, principally pigments, present. The synergy between the kaolin and PCC of the present invention allows for a reduced binder demand compared to comparable prior art pigment compositions as illustrated later.

The binder may mainly or wholly of latex type (i) above. Optionally, a quantity of binder type (ii) or (iii) may be included together with type (i). For example, the type (iii) binder may, together with type



-15-

(i) binder, optionally be used, on an active basis, in an amount of up to 10% by weight, eg from 0% to 5%, especially from 0 to 3%, eg from 1% to 2%, based on the dry weight of the pigment material.

5       The coating composition according to the second aspect of the invention thus contains as principal ingredients water, binder and the pigment composition of the invention (in its first aspect). The amount of water present is a suitable amount required to make the  
10 composition fluid and runnable. Such an amount will depend on the nature of the other generally solid ingredients present, but will generally be between 20% and 40% by weight of the composition. Other ingredients in minor amounts, e.g. in total less than 5% by weight  
15 may be incorporated in the coating composition to improve the properties of the composition. These additional ingredients and the typical quantities required are well known by those skilled in the paper coating art. The additional ingredients may include, for example, one or  
20 more of pigment dispersant (dispersing agent) and lubricity/calendering aid, e.g. solid lubricant, eg calcium stearate.

      The dispersant optionally employed in the composition according to the second aspect of the present  
25 invention may be selected from any well known in the art, for example it may be a polyelectrolyte, eg a polyacrylate dispersant, e.g. sodium polyacrylate. The dispersant may be present, on an active basis, in an amount of from 0.01% to 1% by weight, e.g. from 0.05% to

0.5% by weight, based on the dry weight of the pigments present.

A solid lubricant may also optionally be added to the coating formulation, on an active basis, in an amount of up to 3% by weight, e.g. from 0.1% to 1% by weight, based on the dry weight of pigments.

Further additional ingredients which may optionally be employed in the coating composition include optical brightening agents (OBA's), activators, cross linkers, water retention aids, viscosity modifiers or thickeners, antifoamers/defoamers, dry or wet pick improvement additives, dry or wet rub improvement and abrasion resistance additives, gloss-ink hold-out additives, fluorescent whitening agents (FWA), dyes, biocides/spoilage control agents, levelling and evening aids, grease and oil resistance additives, water resistance additives and insolubilizer and these may be added in amounts well known in the paper coating art.

The paper product to be coated in the method according to the third aspect of the invention may be chosen from any of the paper products well known by those skilled in the art as being suitable for coating by binder and pigment containing aqueous compositions. Such products will comprise on the surface to be coated or in an underlying base sheet or structure a mixture of cellulose fibres usually plus particulate fillers. The paper product may for example be a paper sheet or a packaging or board product, especially a freesheet or a solid bleached sulfite paper product.

-17-

The paper products which are coated using the method according to the third aspect of the present invention may be uncoated or they may carry one or more previously applied coating layers. The previously applied layer(s) may or may not be the same as that applied in the method.

Methods of coating paper and other sheet materials are widely published and well known. For example, there is a review of such methods published in Pulp and Paper International, May 1994, page 18 et seq. Sheets may be coated on the sheet forming machine, ie "on-machine", or "off-machine" on a coater or coating machine. Use of high solids compositions is desirable in the coating method because it leaves less water to evaporate subsequently. However, as is well known in the art, the solids level should not be so high that high viscosity and levelling problems are introduced.

All known methods of coating for use in coating paper using the coating formulation according to the third aspect of the present invention require (I) a means of applying the coating formulation to the material to be coated, viz. an applicator; and (II) a means for ensuring that a correct level of coating formulation is applied, viz. a metering device. When an excess of coating formulation is applied to the applicator, the metering device is downstream of it. Alternatively, the correct amount of coating formulation may be applied to the applicator by the metering device, eg as a film press. At the points of coating application and metering, the paper web support ranges from a backing roll, eg via one

-18-

or two applicators, to nothing (ie just tension). The time the coating is in contact with the paper before the excess is finally removed is the dwell time - and this may be short, long or variable.

5 The coating is usually added by a coating head at a coating station. According to the quality desired, paper grades are uncoated, single coated, double coated and even triple coated. When providing more than one coat, the initial coat (precoat) may have a cheaper  
10 formulation. A coater that is applying a double coating, ie a coating on each side of the paper, will have two or four coating heads, depending on the number of sides coated by each head. Most coating heads coat only one side at a time, but some roll coaters (eg film press,  
15 gate roll, size press) coat both sides in one pass.

Examples of known coaters which may be employed in coating of a sheet material using a composition according to the second aspect of the invention include air knife coaters, blade coaters, rod coaters, bar coaters, multi-  
20 head coaters, roll coaters, roll/blade coaters, cast coaters, laboratory coaters, gravure coaters, kiss coaters, liquid application systems, reverse roll coaters and extrusion coaters.

The coated paper product prepared by the method of  
25 the third aspect of the present invention may have a brightness of at least 75 units, eg from 75 to 95 ISO units, e.g. at least 81 ISO units.

The coated paper product prepared by the method of the third aspect of the present invention may have a  
30 sheet gloss, measured according to the TAPPI standard 75

degree gloss method, of at least 60 units, e.g. at least 65 units, e.g. from 65 to 75 units.

The coated paper product prepared by the method of the fourth aspect of the present invention may have a print gloss, measured according to the TAPPI 75 degree gloss method using black offset ink and a standard print density of 1.6, of at least 85 units, eg from 93 to 99 units.

The coating of the coated paper product prepared by the method of the second aspect of the present invention may have a pore volume of at least  $5\text{cm}^3.\text{kg}^{-1}$ , eg from 5 to  $15\text{cm}^3.\text{kg}^{-1}$ .

The coating of the coated paper product prepared according to the method of the third aspect of the present invention may have an average pore radius of at least 30nm, eg from 30 to 45nm, eg at least 35nm.

The coating of the coated paper product prepared according to the method of the third aspect of the present invention may have a surface micro roughness measured (in the manner described later) using an atomic force microscope of less than  $0.100\mu\text{m}$ , e.g. from  $0.050\mu\text{m}$  to  $0.085\mu\text{m}$ . The fine pigments of the composition according to the first aspect of the invention create such a microscopically smooth surface on the coated paper product which significantly improves the sheet gloss of the coating as well as the brightness thereof.

#### **DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS OF THE INVENTION.**

Embodiments of the present invention will now be described by way of example with reference to the

-20-

following Examples which include, for comparison purposes, examples of prior art procedures.

**EXAMPLE 1**

A pigment composition embodying the invention was prepared using an ultrafine kaolin, herein "Kaolin A" and a fine rhombohedral PCC, herein "PCC A" with a low ratio, i.e. 40:60, of the amount by weight of kaolin to the amount by weight of calcium carbonate in the composition.

Kaolin A has the following properties:

- 10 i) GE brightness: 90.9;
- ii) Specific surface area: 23 meters squared per gram;
- iii) Shape factor: 8;
- iv) Median particle size: 0.18 microns;
- 15 v) Particle size properties (x and P as defined earlier):

	X (micron)	P (%)
	2	99
20	1	99
	0.5	94
	0.25	69

PCC A has the following properties:

- 25 (i) GE brightness: 95
- (ii) Median particle size: 0.5 microns;
- (iii) Particle size properties (x and P defined earlier):

	X (microns)	P (%)
	2	98
30	1	92

-21-

0.5	48
0.25	12

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A coating composition was made using the pigment composition together with water and a binder system. The coating composition contained as a binder system 16% by weight, on an active basis, of a styrene acrylic copolymer latex, based on the dry weight of the minerals and 1.5% by weight, on an active basis, of Protein Technologies Procote 2500 protein, based on the dry weight of the pigments present. The composition also contained 0.5% by weight, on an active basis, based on the dry weight of the minerals of Nopcote C-104, a calcium stearate lubricant and 0.1% by weight, on an active basis, based on the dry weight of the pigments of a sodium polyacrylate dispersant.

The coating composition was made down, i.e. formed into an aqueous suspension, at a target pH of 8,5 - 9.0 at a solids concentration which was the highest able to give the suspension an acceptable runnability, measured as a Brookfield viscosity of from 2500 to 3000mPa.s at 20rpm and a temperature of 22C.

The coating composition was applied to a pre-coated SBS base sheet of North American origin using a laboratory coating machine. The coating composition was applied to a surface of the base sheet so as to give a target coat weight of  $12\text{g.m}^{-2}$ . The coater speed was kept constant at  $400\text{m.minute}^{-1}$  ( $6.7\text{m.s}^{-1}$ ). The coated sheet produced was calendered using a Beloit 750 lab calendar using the calendering conditions of 150°F (66°C), 300 PLI

-22-

(pounds per linear inch) ( $5200\text{kg.m}^{-1}$ ), 25 fpm (feet per minute) ( $0.13\text{m.s}^{-1}$ ), and 2 nips.

The coated, calendered sheets were then tested for physical and optical properties using standard testing procedures.

The sheet and print gloss were measured using a laser goniophotometer. In this type of measurement a laser beam is reflected off a surface and the angular intensity distribution of the specularly reflected light is measured. The measurement device uses a red HeNe laser with a wavelength of 632.8nm and a beam diameter of 0.8mm. The beam was used at an incidence angle of 75 degrees from the surface normal for direct comparison to 75 degree TAPPI gloss measurements. The ISO sheet brightness, or percentage reflectance to violet light of the coated paper, was measured in a manner well known to those skilled in the art using a Technidyne Micro TB-1C brightness meter.

The results are shown in Table 1 later.

## 20 EXAMPLE 2

A pigment composition embodying the invention was prepared using Kaolin A as in Example 1 and a fine aragonite PCC, herein "PCC B" with a low ratio of the amount of kaolin to the amount of calcium carbonate in the composition.

PCC B employed in this composition has the following properties:

- (i) GE brightness: 93
- (ii) Median particle size 0.34 microns;



(iii) Particle size properties (x and P as defined earlier):

	X (microns)	P (%)
5	2	96
	1	83
	0.5	67
	0.25	28

10 A coating composition was prepared in the same manner as described in Example 1 using this pigment composition. The coating composition resulting was calendered and applied to a base sheet as used in Example 1 in the manner described in Example 1 and the properties  
15 of the coated sheet were measured as in Example 1.

The results are given in Table 1 later.

#### EXAMPLE 3

As a comparative example, a pigment composition was prepared as in Example 1 except that the composition was  
20 formed as a blend of another kaolin, 'Kaolin B' and a ground calcium carbonate 'GCC A' in a weight ratio of 60 parts Kaolin B to 40 parts GCC A.

Kaolin A has a GE brightness of 90.8 and a median particle size of 0.45 microns. GCC A has a GE brightness  
25 of 97 and a median particle size of 0.7 microns.

A coating composition using this pigment composition was prepared as described in Example 1 and sheets using this coating composition were prepared and their properties measured as in Example 1. The results are  
30 shown in Table 1 as follows.

TABLE 1

-24-

Example	1	2	3
	(invention)	(invention)	(comp.)
ISO sheet brightness	81.2	81.3	80.8
75 degrees	70.2	72.6	60.1
5 TAPPI Sheet gloss			

As seen in Table 1 the compositions of the invention unexpectedly give a superior combination of sheet  
10 brightness and gloss.

**EXAMPLE 4**

A further coating composition embodying the invention was made in the manner described in Example 1 using as pigment composition, 'P4A', a blend of Kaolin A  
15 and PCC B, both as described earlier, in a weight ratio of 25:75 (kaolin:PCC). The ISO brightness and sheet gloss of paper sheets coated as in Example 1 were measured as described in that Example.

For comparison purposes, the experiment was repeated  
20 except that a commercially available ground calcium carbonate 'GCC B' was used in place of PCC B in a pigment composition P4B.

GCC B has the following properties:

- (i) a GE brightness of 95;
  - 25 (ii) a median particle size of 0.42 microns;
- The results obtained are given in Table 2 as follows.

**TABLE 2**

Pigment composition	Sheet brightness (ISO)	Sheet gloss at 75 degrees
30 P4A (invention)	82.1	71

P4B (comparative)	81.3	68
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As seen in Table 2, both sheet brightness and sheet gloss are beneficially improved by use of the pigment composition embodying the invention, P4A. This is surprising, since the carbonate used in the comparative pigment composition P4B has a higher powder brightness than that used in composition P4A embodying the invention.

The BET surface areas of each of pigment compositions P4A and P4B were measured. Compositions P4A and P4B were found respectively to have specific surface areas of 16 and 20 meters squared per gram. Beneficially, Composition P4A was found to have, in consequence, a reduced binder demand in a coating composition.

**CLAIMS**

We claim:

1. A pigment composition for use in coating a paper product, comprising a blend of at least two particulate inorganic materials comprising (a) a high brightness ultrafine kaolin produced from a blocky kaolin clay, the kaolin having a median particle size less than about 0.5 microns ( $\mu\text{m}$ ) and (b) a fine coating precipitated calcium carbonate (PCC) having a median particle size less than about 0.8 microns, the ratio by weight of the PCC to the kaolin being greater than 1.0.
2. The pigment composition of claim 1 wherein at least 50% of said PCC has an aragonite crystal morphology.
- 15 3. The pigment composition of claim 1 wherein at least 50% of said PCC has a rhombohedral crystal morphology.
4. The pigment composition of claim 1 wherein said 20 kaolin has a median particle size of between about 0.1 and about 0.3 microns and said PCC has a median particle size of less than about 0.55 microns.
5. The pigment composition of claim 2 wherein said PCC 25 has a median particle size of between about 0.25 and about 0.45 microns.
6. The pigment composition of claim 3 wherein said PCC has a median particle size of between about 0.35 and 30 about 0.55 microns.

-27-

7. The pigment composition of claim 1 wherein said kaolin comprises greater than 55% by weight of particles having a particle size of less than 0.25 microns.

5 8. The pigment composition of claim 1 wherein said kaolin has a particle shape factor of 15 or less.

9. The pigment composition of claim 1 wherein the percentage by weight of said kaolin in said pigment  
10 composition is in the range from about 10% to about 45% by weight and the percentage by weight of said PCC in said pigment composition is in the range from between about 55% to about 90%.

15 10. A paper product coating composition comprising an aqueous suspension of the pigment composition of claim 1 and a binder.

11. The coating composition of claim 10 wherein said  
20 coating composition contains a pigment dispersant.

12. The coating composition of claim 10 wherein said coating formulation contains a lubricant.

25 13. A method for coating a paper product by applying the coating composition of claim 10 to coat a surface of the paper product.

14. The method of claim 13 wherein said paper product is  
30 a solid bleached sulfite paper product.

-28-

15. A method of improving the optical and printing properties of a paper product, comprising adding the pigment composition of claim 1 to an aqueous suspension comprising a binder to form a runnable coating composition and applying said coating composition to at least one surface of said paper product.

16. The method of claim 16 wherein said paper product is a solid bleached sulfite paper product.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/10824

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) :C04B 14/02, 14/10, 14/28; C09C 1/02, 1/42

US CL :106/416, 464, 468, 486, 487; 162/181.1, 181.8

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/416, 464, 468, 486, 487; 162/181.1, 181.8

IPC(7): 14/02, 14/10, 14/28; C09C 1/02, 1/42

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,833,747 A (BLEAKLEY ET AL.) 10 November 1998 (10/11/98), see column 1, line 3-column 6, line 40.	1-16
Y	US 5,478,388 A (GANE ET AL.) 26 December 1995 (26/12/95), see column 3, line 33-column 6, line 60.	1-16
Y,E	US 6,074,474 A (BROOME ET AL.) 13 June 2000 (13/06/00), see column 3, lines 40-56 and the claims.	1-9
Y	US 5,879,512 A (McGENITY ET AL.) 09 March 1999 (09/03/99), see column 1, line 65-column 2, line 8	12
Y	US 5,749,958 A (BEHL ET AL.) 12 May 1998 (12/05/98), see the claims.	1,4,7,8

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 21 JUNE 2000	Date of mailing of the international search report <b>14 AUG 2000</b>
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